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(56) Documents Cited

GB 2053948 A

GB 1524881 A

GB 1513701 A

GB 1509941 A

GB 0915913 A

(58) Field of Search

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(54) **Inks**

(57) An ink-jet ink comprising colourant, binder and solvent is characterised in that the solvent is a mixture of 60 - 76% by volume ethanol and 40 - 24% by volume water.

When the binder is hydroxypropylcellulose and the colourant is erythrosine the ink can be used to form boil resistant deposits on eggshells.

GB 2 277 094 A

INKSField of the Invention

5 This invention relates to ink-jet inks and to their use.

Background of the Invention

10 Ink-jet inks must meet many criteria, including fast drying, low viscosity and, at least for continuous ink-jet printing, low electrical resistivity. GB-A-2053948 (A.B. Dick) indicates some constraints on the nature of ink-jet inks, and typical properties of such inks.

15 For these reasons, and to provide all the ingredients, i.e. colourant, polymeric binder and usually also conductive salt in solution, volatile organic solvents such as MEK (methyl ethyl ketone) have been widely used. In particular, the high volatility of such solvents allows the ink to dry rapidly, and suitable binders ensure that the ink adheres stably to the substrate being printed.

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 There is now environmental pressure to avoid the use of solvents such as MEK. This is particularly true in food-printing applications. However, it is difficult to find an adequate replacement, owing to the more limited choice of components that are soluble in alternative solvents, and to their generally lower volatility.

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 GB-A-2053948 discloses an ink-jet ink that has a pH of 7 to 10.5 containing colourant, styrene-(alkyl)acrylic acid copolymer resin, usually also a plasticiser and a modifying resin that improves adhesion of the ink to the substrate, and water/C₁₋₃alkanol (in a ratio of 9:1 to 2:8 w/w) as the solvent. In the specific Examples, the alkanol is methanol or n-propanol.

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WO-A-9214795 (Willett International Limited)

describes an ink-jet ink composition for use in printing onto foodstuffs. The use of alkanol/water mixtures of above 50% by weight alcohol is described as unsatisfactory, e.g. owing to spreading of the printed image on a substrate and precipitation of dyestuffs, Willett use acetone instead of alcohol. Example 1 of this specification discloses an ink composition comprising acetone, water (3:1 w/w), erythrosine, Patent Blue and hydroxypropylcellulose, for printing onto foodstuffs, e.g. eggshells. The ink of Example 3 comprises acetone, water, erythrosine, Patent Blue, and shellac in solution in ethanol. For successful dissolution of the shellac, the acetone:water:ethanol ratio is 46.8:21:10-20 w/w. This ink, again apparently suitable for printing onto eggshells, is also reported as boil-resistant.

Summary of the Invention

According to the present invention, an ink-jet ink comprises a colourant, a polymeric binder for the ink, and a solvent comprising a mixture of 60-76% v/v ethanol and 40-24% v/v water. The novel ink complies with UK and EC legislation, specifically SI 1992 No. 165; 30 January 1992 and proposed EC Directive 'Com (92) 255 final-Syn424; 17 June 1992. It is therefore suitable for food use. This ink is suitable for use in printing onto eggshells, and the solvent mixture is self-sterilising. The ink is also stable.

Where it is desired that the ink should be boil resistant we have found that the colourant and the binder needs to be selected with care.

Erythrosine with hydroxypropyl cellulose of molecular weight 95,000 provides a boil resistant deposit.

Description of the Invention

The novel ink has a viscosity that satisfies the requirements for ink-jet printing. It may be selected by the choice of components that are used, and their amounts.

The colourant may be a dye, which is preferably water soluble or pigment, which is preferably water-dispersable. Many water-soluble food-grade dyestuffs are known, and may be suitable for use in the present invention. Erythrosine is a particularly suitable example, being a fluoresceine derivative that is also a salt; its salt nature provides the conductive component that is required for continuous ink-jet printing. Erythrosine also has good binding power.

Many colours are permitted for food use but we prefer E127 erythrosine when a deposit which is to be boil resistant is required.

The following is a list of food grade colour which may preferably be used when boil resistance is not required.

| EEC No. | Common Name | Colour Index* or Description |
|---------|--------------------------------------|------------------------------|
| E 102 | Tartrazine | 19140 |
| E 104 | Quinoline Yellow | 47005 |
| E 110 | Sunset Yellow FCF Orange Yellow S | 15985 |
| E 120 | Cochineal, Carminic acid Carmines | 75470 |
| E 122 | Azorubine, Carmoisine | 14720 |
| E 123 | Amaranth | 16185 |
| E 124 | Ponceau 4R, Cochineal Red A | 16255 |
| E 127 | Erythrosine | 45430 |
| E 128 | Red 2G | 18050 |
| E 129 | Allura Red AC | 16035 |
| E 131 | Patent Blue V | 42051 |
| E 132 | Indigotine, Indigo Carmine | 73015 |
| E 133 | Brilliant Blue FCF | 42090 |
| E 142 | Green S | 44090 |
| E 151 | Brilliant Black BN, Black PN | 28440 |
| E 154 | Brown FK | - |
| E 155 | Brown HT | 20285 |
| E 162 | Beetroot Red, betanin | - |

* number from 3rd Ed. 1982, vols 1-7, 1315.

Aluminium lakes prepared from the colours mentioned above may also be used.

Many binders are known for use in ink-jet inks. For use in the present invention, the binder, like the other components of the ink, should be a food-grade material. It may also have thickening and/or film-forming properties. It may be a cellulosic material, e.g.

hydroxypropyl-cellulose.

Hydroxyalkyl celluloses have been found satisfactory in the solvent system of the present invention. The binder should be tested for suitability by being dissolved in water and then ethanol should be added slowly with vigorous stirring up to 76% by volume to give a final solution viscosity at 25°C of 3 to 10 centipoise (M.Pa). If the binder precipitates out or produces a gelatinous system, then the binder will not be suitable. When such effects occur they render drop formation unpredictable.

Examples of the cellulose binders are E 460, either as powdered or microcrystalline cellulose; E 461, methyl cellulose; E 464, hydroxypropyl methyl cellulose; E 465 ethyl methyl cellulose; and E 466, carboxymethyl cellulose.

We prefer to use hydroxypropyl celluloses of molecular weights in the range 40,000 to 140,000 subject to the above test; those with molecular weights of 100,000 and below give the best results.

As indicated above, the amounts of the various components will be determined primarily by the ability to use the ink in an ink-jet printer, and to obtain a satisfactory image on the substrate. While the solvent is the major component of the ink, the ink composition suitably contains 0.01 or 0.05 to 20%, preferably 0.1 to 20% or 0.1 to 10%, more preferably 0.5 to 5% by weight of the binder; the amount of colourant may be in a similar range.

The following Examples illustrate the invention.

Example 1

5 A solvent blend was prepared, comprising 76% by volume ethanol and 24% by volume water. To one litre of the solvent blend were added 5.7 g of hydroxypropyl-cellulose (0.56% by weight) (grade LF, molecular weight 95,000) and 9.0 g of erythrosine (0.88% by weight) (FD & C certified).

10 The resultant composition was suitable for use in a continuous ink-jet printer. Satisfactory images were obtained on eggshells, while meeting all UK and EC egg-marking regulations. The printed image is boil-resistant. The ink is self-sterilising and chemically-stable.

15 Example 2

Example 1 was repeated except that the solvent blend was 60% by volume ethanol and 40% by volume water.

Similar results were obtained to those of Example 1.

CLAIMS

1. An ink-jet ink comprising a colourant, a binder, and a solvent characterised in that the solvent is a mixture of 60-76% v/v ethanol and 40-24% v/v water.
2. An ink as claimed in claim 1 characterised in that the binder is a hydroxypropylcellulose.
3. An ink as claimed in claim 1 or claim 2 characterised in that the Colourant is E 104, 110, 120, 122, 123, 124, 127, 128, 129, 131, 132, 133, 142, 151, 154, 155 or 162.
4. An ink as claimed in claim 1 characterised in that the binder is hydroxypropylcellulose of molecular weight 95,000 and the colourant is E 127, erythrosine.
5. A process for printing a substrate, characterised in that it comprises applying an ink as claimed in claim 1, 2, 3 or 4 on to the substrate via an ink-jet printer.
6. A process as claimed in claim 5 characterised in that the substrate is an eggshell.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

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Relevant Technical Fields

- (i) UK Cl (Ed.M) C3V (VAD); C4A
(ii) Int Cl (Ed.5) C09D

Search Examiner
K MACDONALD

Date of completion of Search
19 JULY 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1-6

(ii)

Categories of documents

- | | |
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| <p>X: Document indicating lack of novelty or of inventive step.</p> <p>Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p>A: Document indicating technological background and/or state of the art.</p> | <p>P: Document published on or after the declared priority date but before the filing date of the present application.</p> <p>E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p>&: Member of the same patent family; corresponding document.</p> |
|--|---|

| Category | Identity of document and relevant passages | Relevant to claim(s) |
|----------|--|----------------------|
| X | GB 2053948 A (A B DICK) Claim 1 | At least Claim 1 |
| X | GB 1524881 (A B DICK) Example 3 | At least Claim 1 |
| X | GB 1513701 (CIBA-GEIGY) Claims 1, 3 | At least Claim 1 |
| X | GB 1509941 (KONTOR KEMI) Example 1 | At least Claim 1 |
| X | GB 0915913 (KODAK) Claim 4 | At least Claim 1 |

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).